GRASAS Y ACEITES 74 (3)
July-September 2023, e520
ISSN-L: 0017-3495
https://doi.org/10.3989/gya.0565221

Rapid detection of argan oil adulteration by frying oils using laser induced fluorescence spectroscopy combined with chemometrics tools

S. Farres, L. Srata, M. Chikri, S. Addou and F. Fethi✉

Laboratory of Physics of Matter and Radiations (LPMR), Physics Department, Faculty of Sciences, Mohammed First University Oujda, Morocco
✉Corresponding author: fethi.fouad@yahoo.fr

Submitted: 26 May 2022; Accepted: 07 February 2023; Published online: 10 October 2023

SUMMARY: There is a contentious need for robust and rapid methodologies for maintaining the authenticity of foods. The aim of this study was to detect and quantify argan oil adulteration using Laser Induced Fluorescence (LIF) spectroscopy coupled with chemometric methods. Principal Component Analysis (PCA) and Partial Least Squares Regression (PLSR) were used to assess argan oil authenticity; PCA was used to classify samples according to their quality and the PLS model to determine the amount of adulterants in pure argan oil. The correlation coefficient of the obtained model was about 0.99, with Root Mean Square Error of Prediction (RMSEP) and Standard Error of Prediction (SEP) of 2%. This study demonstrated the feasibility of LIF spectroscopy combined with chemometric tools to identify adulterants in pure argan oil from a percentage of adulteration, of 0.35 % without the need to destruct samples.

KEYWORDS: *Adulteration; Argan oil; Chemometrics; LIF.*

RESUMEN: ***Detección rápida de la adulteración de aceite de argán con aceites de fritura usando espectroscopía de fluorescencia inducida por láser combinada con herramientas quimiométricas***. Existe una necesidad de metodologías sólidas y rápidas para determinar la autenticidad de los alimentos. El objetivo de este estudio es detectar y cuantificar la adulteración del aceite de argán mediante espectroscopia de fluorescencia inducida por láser (LIF) junto con métodos quimiométricos. Se utilizaron el análisis de componentes principales (PCA) y la regresión de mínimos cuadrados parciales (PLSR) para evaluar la autenticidad del aceite de argán. Se utilizó PCA para clasificar las muestras según su calidad y el modelo PLS se aprovechó para determinar la cantidad de adulterantes en el aceite de argán puro. El coeficiente de correlación del modelo obtenido fue de alrededor de 0,99, el error cuadrático medio de la predicción (RMSEP) y el error estándar de predicción (SEP) del 2%. Este estudio demostró la viabilidad de la espectroscopia LIF combinada con herramientas quimiométricas que permiten identificar adulterantes en aceite de argán puro, sin necesidad de destruir muestras, a partir de un porcentaje de adulteración del 0,35 %.

PALABRAS CLAVE: *Aceite de argán; Adulteración; Quimiometría; LIF.*

Citation/Cómo citar este artículo: Farres S, Srata L, Chikri M, Addou S, Fethi F. 2023. Rapid detection of Argan oil adulteration by frying oils using laser induced fluorescence spectroscopy combined with chemometric tools. *Grasas Aceites* **74** (3), e520. https://doi.org/10.3989/gya.0565221

1. INTRODUCTION

Food fraud is when a food is not presented in its authentic form. It can present serious health risks if hazardous materials are added to food products. It can also have an economic impact on consumers for investing in products of inferior quality (Charlebois *et al.,* 2016). Over the last decade, food fraud has been identified as an emerging risk to the food industry and a significant concern to consumers and food regulators (Ulberth, 2020). Among the foods that are subject to fraud is argan oil. This oil is very valuable thanks to its virtues and high price (Ruas *et al.,* 2015). It is one of the oils that has been frequently subjected to adulteration. Sometimes suppliers can adulterate pure argan oil using a low percentage degree of cheap vegetable oils, precisely frying oils, to give acceptable analytical values that can give a favorable quality assessment to the adulterated oil as pure oil. Argan oil is obtained from the fruit of the argan tree. This tree is native to southwestern Morocco, which covers an area of ~829000 ha. Its life span frequently exceeds 200 years (Gonzalez-Fernandez *et al.,* 2020). Moreover, there is a Moroccan regulation, developed in 2003, that manages argan oil according to NM 08.5.090 standards (Moroccan Standard 2003).

This oil is well known for its pharmacological properties and has been used in traditional medicine for centuries. Scientific evidence has inferred from experimental studies that the consumption of argan oil may reduce the risk of disease through a biological mechanism which acts on blood pressure, plasma lipids and antioxidant status (El Midaoui *et al.,* 2016). Thanks to its composition which is rich in antioxidants and monounsaturated and polyunsaturated fatty acids, argan oil could be used in a nutritional prevention setting to prevent the progression of some diseases (ELMostafi *et al.,* 2020). These different actions are ensured by its interesting chemical composition, rich in antioxidants, such as vitamin E, and in particular in gamma tocopherols, as well as the presence of specific polyphenols and sterols (Şekeroğlu *et al.,* 2017).

The demand for high quality and safety in food production obviously calls for high standards of quality and process control (Kharbach *et al.,* 2021), which in turn requires appropriate analytical tools to investigate food. The above discussion clearly gives the importance of finding a way to detect adulteration, so that the quality of argan oil is guaranteed (Kharbach *et al.,* 2021). There are conventional methods used in the detection of adulteration including gas chromatography (Xing *et al.,* 2019), electronic nose and tongue technology (Majchrzak *et al.,* 2018), and UV photo-ionization ion mobility spectrometry (Garrido-Delgado *et al.,* 2018), TR-FTIR spectroscopy (Ozulku *et al.,* 2017), among others. These methods provide high efficiency and sensitivity, and can measure multiple components. However, they are time consuming, expensive and complicated. That is why there is high demand for a sensitive technique that can provide result in less time, without generating waste, at low cost, and without the need for super-qualified personnel. Analytical methods are an important point to consider for both detecting and deterring food fraud (Callao and Ruisánchez, 2018). Thus, the need for rapid, low-cost and confinable analytical methods has motivated the use of spectroscopic techniques associated with chemometrics to characterize oils and fats (Dogruer *et al.,* 2021).

Chemometric methods use multivariate statistic to extract information from complex analytical data (Yang *et al.,* 2005). However, LIF was highlighted as a potential analytical technique for oils and fat characterization because it meets all routine analysis requirements and appears to be the best technique for analyzing oil adulteration. This technique now has the potential to replace or complement classical methods, and a number of works have been reported for detecting vegetable oil adulteration (Addou *et al.,* 2016; Wang and Wan, 2020). LIF is a sensitive, fast, less expensive and non-polluting method of analysis, increasingly used in various fields of product analysis, and food industry to assess quality. It provides information on the presence of fluorescent molecules and their molecular environment within the samples analyzed (Ozaki *et al.,* 2013). Indeed, the fluorescent properties of molecules are very sensitive to changes in their environment. The answer then varies according to the composition and characteristics of the material (Karoui and Blecker, 2011).

In this paper, LIF has been used to determine argan oil adulteration with waste frying oil. A LIF system was assembled in the experiment. Using an Nd: YAG laser beam (532 nm), the fluorescence spectra of mixtures of pure and adulterated argan oil

were measured. The identification of several important vegetable oils and the adulterated concentration were achieved by employing PCA (Chikri *et al.,* 2018; Tipping and Bishop, 1999) and PLS model (Wold *et al.,* 2001; Srata *et al.,* 2019). The prediction errors of adulterated concentration were about 2%. The results can provide reference for the quality identification of argan oil, knowing that the adulteration was carried out using two kinds of adulterants.

2. MATERIALS AND METHODS

2.1. Sample preparation

In this work, argan oil, noted AO, was used to assess its adulteration by two commercial vegetable oils noted VO1 and VO2. VO1 is commercial sunflower oil and VO2 is commercial edible oil sold without any indication of its origin. Cheap vegetable oils (VO1 and VO2) were purchased from a market in Oujda (East of Morocco) and pure argan oil (handmade) was obtained from Agadir (south of Morocco).

The samples were divided into two groups. The first one contained samples of AO adulterated by VO1 (54 samples), and the second one contained AO adulterated by VO2 (55 samples). Cheap oils were heated at 200 °C for 30 minutes many times, until the oil had the same color as AO. VO1 and VO2 were heated for the reason that fraudsters use waste frying oil to adulterate argan, since this oil has the same color as argan oil and the detection of adulteration becomes more difficult. The process of adulteration was achieved as follows: AO was adulterated by VO1 from 0 to 31% and by VO2 from 0 to 32%. A total of 109 samples were prepared. The first sample in each group contained 100% AO and the second one contained 99.6% AO and 0.4% adulterant (VO1 or VO2). The procedure was repeated for all samples, increasing the number of drops of adulterant for each sample by one drop. Therefore, for each sample, a drop of pure AO oil was replaced by a drop of adulterant. The drops were added using a micropipette and masses were measured using a digital scale of very high sensitivity. Finally, the prepared samples were homogenized and stored in the dark at ambient temperature.

2.2. LIF analysis

LIF is a physical phenomenon in which a molecule absorbs an amount of the energy from a laser beam. There is thus a transition from a ground state S_0 to an excited state S_1 with a change in the electron orbital. This excited state S_1 has a very short lifetime (a few nanoseconds). Changes in conformation and interactions with surrounding molecules change the molecule from the excited state S1 to low vibrational levels of S_1: this is the internal conversion. In the case of fluorescent molecules, the transition from the excited state S_1 to the ground state S_0 takes place with the release of a photon of lower energy. This phenomenon is laser induced fluorescence, which occur at wavelengths greater than the incident excitation wavelength (Mazouffre 2009). The LIF system used in this work was an assembled system. The spectral measurement of the LIF technique was obtained by irradiating the samples with an Nd: YAG laser beam (532 nm) set at 2 mW, with 3.3 V DC operating voltage and 0.4 A current. During irradiation, the fluorescence emitted by the samples was collected by an optical fiber (2 m long and 400 µm in diameter), equipped with an SMA type connector at each end. The axis of the optical fiber was positioned at an angle of 90° to the direction of the laser beam in order to collect as much fluorescent signal as possible and avoid the detection of photons from the incident beam. The beam was dispersed by a spectrophotometer Avantes, model USB2000, grating 600 lines, blazed at 750 nm, L2 lens, 100 µm slit, equipped with a 2048-pixel charge coupled detector CCD. It consisted of a linear array of silicon (Si) diode and was linked to a computer by a USB connection in order to visualize the fluorescent spectra of each sample. The spectrophotometer used in this work covered the spectral range 500-1000 nm. Note that the spectra were performed in three replicates, under the same conditions. Analyses were made using the average.

2.3. Data processing

The obtained spectral data were converted into Microsoft Office Excel format for Matlab software analysis. The spectral range was reduced from 500-1000 nm to 540-750 nm. Then, to reduce noise and baseline shifts, the spectra were corrected using preprocessing, whose objectives were the attenuation of non-linearity between variables, the elimination of interference and reduction of random noise (Verboven *et al.,* 2012).

Before multivariate data analysis, all LIF spectra were subjected to Savitzky-Golay smoothing (1 point, 2 orders) then the spectra obtained were subjected to a Multiplicative Scatter Correction (MSC) combined with a second derivative for PCA analysis and combined to Baseline for PLS modeling (Savitzky and Golay, 1964; Zheng *et al.,* 2015). MSC is a diffusion correction method that was introduced in 1983 and developed in 1985 (Guidetti *et al.,* 2012). It is based on the idea of correcting the level of dispersion of all sample spectra from an "ideal" spectrum, which is usually the average spectrum. The concept behind MSC is that artifacts or imperfections will be removed from the data matrix (spectra) prior to modeling. The MSC consists of two steps:

- Estimation of the correction coefficients (additive and multiplicative contributions): Each spectrum x_j^{LIF} is then estimated with respect to the average spectrum of all the spectra considered $\bar{x}^{LIF} = \sum_{j=1}^{J} \frac{x_j^{LIF}}{j}$ by a method of least squares.

$$x_j^{LIF} = a_j + b_j \overline{x^{LIF}} + e_j$$

- Correction of recorded spectrum:

$$x_{MSC\,j}^{LIF} = x_j^{LIF} - \frac{a_j}{b_j} = \bar{x}^{LIF} + \frac{e_j}{b_j}$$

e_j: represents the spectrum of the residues

$x_{MSC\,j}^{LIF}$: corrected spectrum

a_j and b_j are the correction coefficients that can be estimated by a least squares method.

The first and second derivatives are used for baseline variation reduction and separation of overlapping bands, so hidden bands are enhanced. With regards to baseline preprocessing, most correction methods make the supposition that the observed spectrum is the combination of a useful signal and a signal of uncontrolled variation. Therefore, the correction consists of subtracting the background from the obtained signal.

2.4. Data analysis

The wavelength range used for LIF analysis was reduced to 540 - 750 nm to keep only the part that contains relevant information and to eliminate noise. PCA was exploited to get main information from spectra and reduce the number of variables. Then PLS algorithm was applied on LIF spectra to establish a model that can predict the percentage of adulteration. PLS calibration gives optimum results compared to many other multivariate calibration methods. An important aspect of PLSR is that it collects the relevant spectral information in a few linear combinations of the spectral measurements. These combinations or components can be used to facilitate interpretation of the relationship between concentrations and spectra as well as the relationships among the spectral variables themselves.

The samples were divided into calibration/ validation and prediction datasets. The optimum number of latent variables was obtained using the full cross validation method. The prediction performance of each model was evaluated throughout the root mean square error (which represents the standard deviation of the residuals), the prediction standard errors, and the coefficient of determination (R^2) of both calibration and validation data sets. In general, as low as the RMSEC/P and SEC/P values can be, and R^2 as close as possible to 1, the better the model's predictions will be. Equations corresponding to each parameter are:

$$R = \frac{\frac{\sum_i (y_i - y)(y_i' - y_i)}{N-1}}{\sqrt{\frac{\sum_i (y_i' - y')}{N-1}} - \sqrt{\frac{\sum_i (y_i - y)}{N-1}}}$$

$$RMSEC = \frac{1}{I_C} \sum_{i=1}^{I_C} (\hat{y}_i - y_i)^2$$

$$SEC = \sqrt{\frac{\sum_{i=1}^{i_p} (\hat{y}_i - y_i)^2}{I_c - 1}}$$

$$RMSEP = \frac{1}{I_P} \sum_{i=1}^{I_P} (\hat{y}_i - y_i)^2$$

$$SEP = \sqrt{\frac{\sum_{i=1}^{i_p} (\hat{y}_i - y_i - bias)^2}{I_p - 1}}$$

$$Bias = \frac{\sum_{i=1}^{I_p} (\hat{y}_i - y_i)^2}{I_p}$$

Where:

$\hat{y}_i$ = the predicted value of the ith observation.

y_i = the measured value of the ith observation.

I_C = number of observations in the calibration set.

I_P = number of observations in the validation set.

3. RESULTS AND DISCUSSION

3.1. Spectral characteristics

Figure 1 shows an overlay of LIF spectra of AO, VO1 and VO2 oils. The spectrum of VO2 oil showed emission at around 650 - 700 nm, This emission was due to the fluorescence of chlorophyll compounds. The AO spectrum showed a fluorescent band around 550 - 625 nm, although this emission was practically absent from the VO1 and VO2 spectra. Figure 2 represents LIF spectra of the same samples after heating VO1 and VO2. The spectra showed the same shape with different intensity. In this figure, the absence of the peak in the red region 650 - 700 nm could be observed, which means the absence of chlorophyll compound emission. It can be concluded from Figures 1 and 2 that heating produced the degradation of the Chlorophyll.

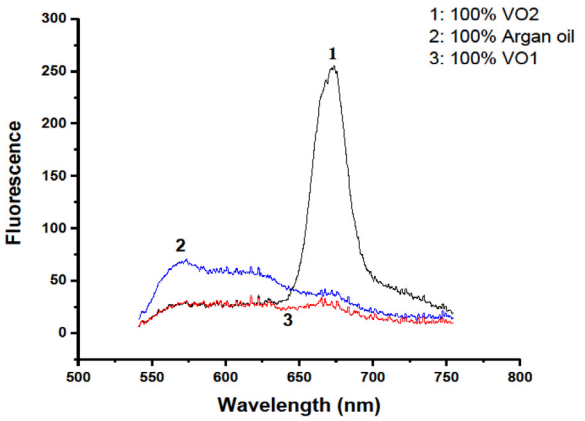

FIGURE 1. Laser induced fluorescent spectra of pure argan oil, VO1 and VO2 samples before heating without any pretreatments. VO: Commercial vegetable oil.

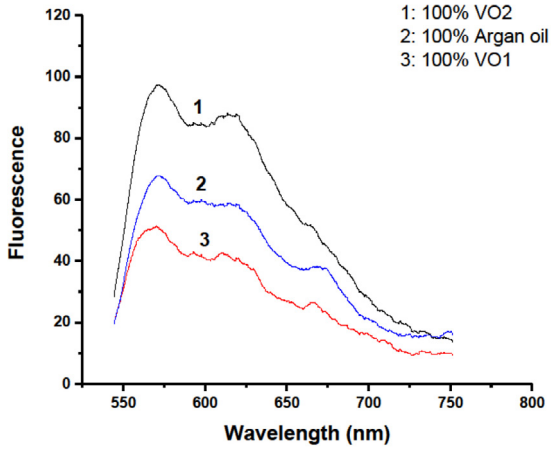

FIGURE 2. Laser induced fluorescent spectra of argan oil, VO1 and VO2 samples after heating without any pretreatments. VO: Commercial vegetable oil.

Figure 3 shows seven spectra in the spectral range of 544 - 750 nm. The first spectrum correspond to AO's fluorescence and the other spectra represent the fluorescence of the adulterated samples, showing the tendency of the spectra according to the concentrations of adulterant. It can be seen from Figure 3 that the spectra are similar to each other and they are a bit noisy. A vertical baseline shift and intensity difference between the spectra can also be seen. Actually, when an oil sample is adulterated, whether the amount of adulterant is small or large, the whole spectrum of the pure sample is affected. These deformations are corrected using chemometric pretreatments. In order to reduce variability in the spectra and improve the signal-to-noise ratio, the spectra were fitted using smoothing preprocessing and then MSC combined to the second derivative (Savistky - Golay) was applied as a suitable preprocessing for PCA analysis and MSC combined to the baseline for PLS analysis. After the spectra were pretreated, chemometric methods were used to extract hidden information.

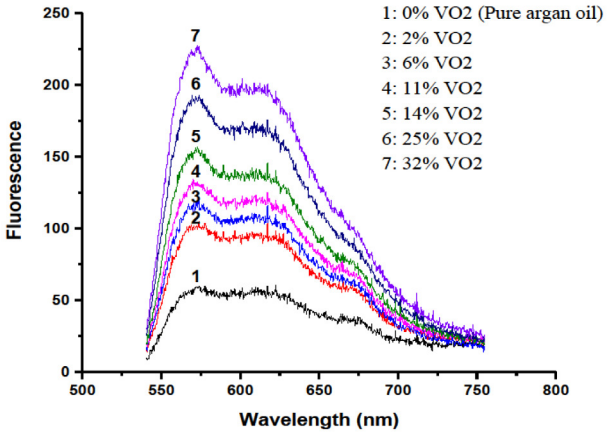

FIGURE 3. Laser induced fluorescent spectra of some adulterated argan oil samples showing the tendency of spectra according to adulterant concentrations from 0 to 32% in the spectral range 540 –750 nm.

3.2. PCA results

After preprocessing the spectra using smoothing combined to MSC and the second derivative, PCA was performed to explore the similarities and differences in samples, to extract relevant information and reduce the number of variables. Figure 4 presents the score plot of PCA applied to LIF spectra. A total 109 samples were measured in this work. The first two principal components accounted for

approximately 73% of the total variability in the data. PC1 explained 72% of the total variance and 1% of the information was explained according to PC2. The interpretation of the results was made via loading plots; they describe how much each variable contributes to a particular principal component. Large loadings (positive or negative) indicate that a particular variable has a strong relationship to a particular principal component. There was a strong relationship between noise in the loadings and the optimal number of components. The concepts of underfitting, overfitting and optimal prediction ability have an important connection to the shape of loading plots, which can be seen when plotting loadings versus wavelength number for all the components computed. For the first few components corresponding to the largest eigenvalues, the shapes of these plots looked like spectra, but as we went towards the components with smaller eigenvalue, we introduced more and more noise (overfitting) and this is sometimes clearly seen as ripples and irregularities in the loading plots. There was a tendency, that close to the optimal number of components, the noise started to become clearly visible in these plots.

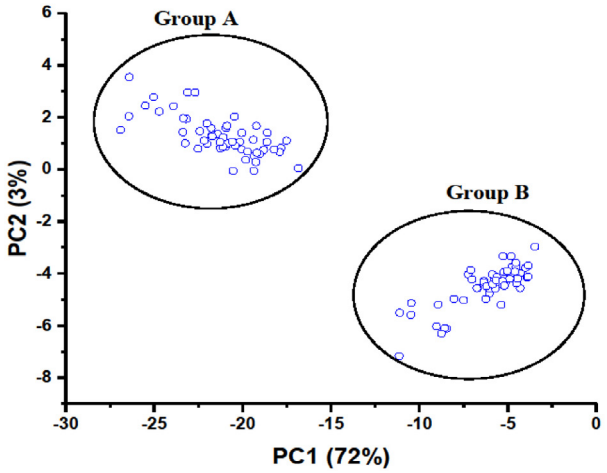

Figure 4. Bi-dimensional score plots of PC1 and PC2 vectors of 109 adulterated argan oil samples. Group A: Argan oil samples adulterated by VO1. Group B: samples of Argan oil adulterated by VO2. PC: Principal component, VO: Commercial vegetable oil.

After applying PCA to the pretreated spectra, samples were significantly classified. It can be seen from Figure 4 that PCA can distinguish samples from each other successfully. Adulterated argan oils are different after passing through the PCA process, and it can be seen from the figure that objects were dispersed according to a two-dimensional space (PC1 and PC2) and divided into two sets according to the type of adulterants. The lower right group in the score graph consists of AO samples adulterated with VO2, noted group B and the higher left group consists of AO samples adulterated with VO1, noted group A. By projecting samples according to PC1, it can be easily noticed that the first component contained information which was responsible for the separation between samples; a low separation existed by projecting samples according to PC2. Group B is located in the negative part of PC2 and group A is located in the positive part of PC2. It can be concluded that, by this model, it was possible to determine the type of adulterant for an unknown sample by taking its spectrum and injecting it into this model.

3.3. PLS result

PLS was exploited as a multivariate calibration technique. It constructs a mathematical model based on the features of PCA and multiple regression to find a linear mathematical relationship between two datasets, X (spectra) and Y (level of adulteration) (Morsy and Sun, 2013).

The spectral data were arranged in a 2D matrix (X), the rows of this matrix represent the samples (109 samples) and the columns contain the number of variables. One column vector (Y) containing the concentration of each adulterant was added to this matrix and the data were then analyzed. To make sure that the obtained model was neither over nor underfit, a cross validation using the leave-one-out method was considered. The linearity of the regression model was evaluated by fitting the reference adulteration value against the predicted ones.

The above PCA model successfully identified the type of cheap edible oil added to AO. To further predict the contents of VO1 and VO2 in the blended oil samples, PLS regression was performed. This method has been successfully used in several studies to predict the percentage of adulterants in oils. PLS regression was applied on raw and pretreated spectra and the one that gave the best result was kept. In this work, LIF data were preprocessed by taking a smoothing (1 point) combined to MSC and Baseline. After removing the outliers, the set of samples was randomly divided into three sample sets samples, in which two sets were used as the experimental group, calibration/validation sets, containing almost 85% of

the total set of samples (70% calibration, 15 % validation) and one set as the testing group containing the 15% remaining.

The efficiency of the calibration model can be determined generally from three statistical parameters: the correlation (R), the standard error of calibration (SEC) and the mean square error of calibration (RMSEC). a R value greater than 0.9 indicates a good response for the parameter studied and less than 0.7 indicates a poor response. When a new spectrum is inserted into the matrix, it is compared to the spectral basis, the closest spectrum is then used to make a PLS regression.

The graphic display of the calibration/validation and prediction produced using the PLS model with the best performances is shown in Figure 5. The calibration results of 109 samples using PLSR produced excellent overall models with a correlation greater than 0.99 and low values for RMSEC and SEC. The same was true for the predicted model. It gave excellent statistical values with a correlation of 0.92, RMSEP and SEP of about 2%. The results indicate that the method proposed in this work is feasible for the detection and quantification of argan oil adulteration by cheap vegetable oils. Table 1 shows all the statistical results of the calibration and prediction models. A similar study was

TABLE 1. Results of the PLS regression model for the LIF data matrix.

Calibration			Prediction		
Correlation	SEC	RMSEC	Correlation	SEP	RMSEP
0.99	2.25	2.23	0.92	2.40	2.38

SEC: Standard Error of Calibration, RMSEC: Root Mean Squares Error of Calibration, SEP: Standard Error of Prediction, RMSEP: Root Mean Squares Error of Prediction. Each value in the table represents the result of three repeated measurements.

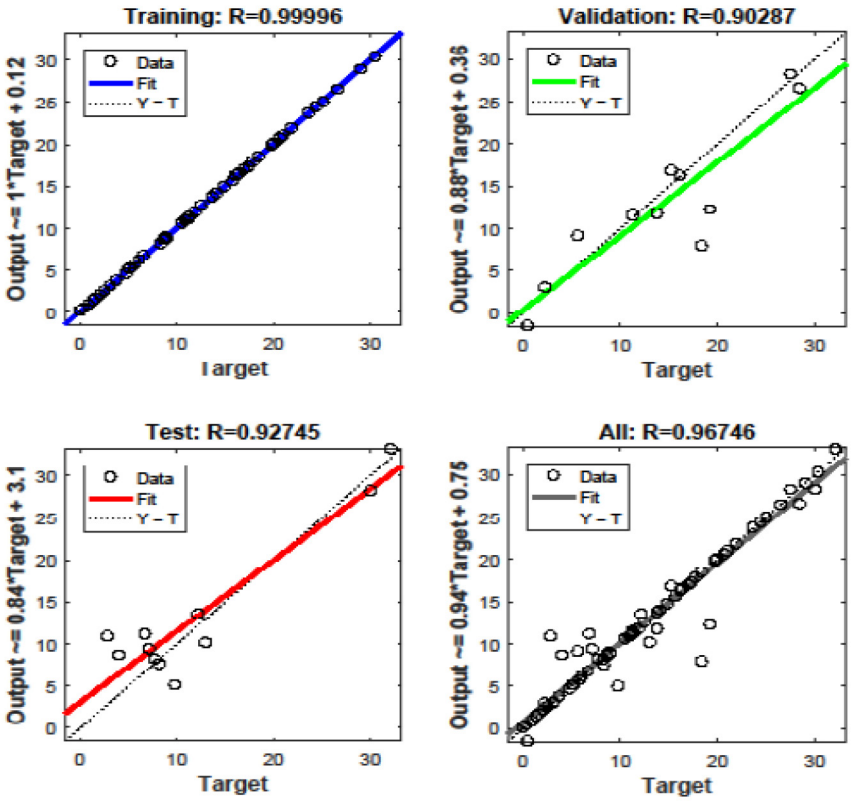

FIGURE 5. Training, validation and testing models of 109 samples in the spectral range 540 –750 nm. The model shows the best prediction accuracy.

published using near infrared spectroscopy to evaluate the adulteration of argan oil by cheap oils (Farres *et al.,* 2019). When comparing the results obtained in this work to those obtained in the published study, it can be easily seen that the R value is higher and error values are low. Therefore, it can be concluded that LIF spectroscopy was revealed to be most suitable technique to study the adulteration of argan oil, especially since both techniques were carried out on the same samples. Table 2 groups together the results obtained using near infrared spectroscopy (published work) and laser-induced fluorescence spectroscopy.

TABLE 2. Statistical parameters of PLS regression models for the adulteration of argan oil using two different spectroscopic methods.

	Laser Induced Fluorescence	Near Infrared Spectroscopy
Correlation	0.99	0.92
SEC	2.25	3.22
RMSEC	2.23	3.24

SEC: Standard Error of Calibration, RMSEC: Root Mean Squares Error of Calibration.

To prove the efficiency of these models, they were tested on two non-synthetic samples and the results are shown in Figure 6. Two non-synthetically adulterated samples were inserted into the PCA model, and as can be seen from the figure, one of samples was close to group A, and the second one was close to group B. This mean that the first sample was adulterated by VO1 and the second one with VO2.

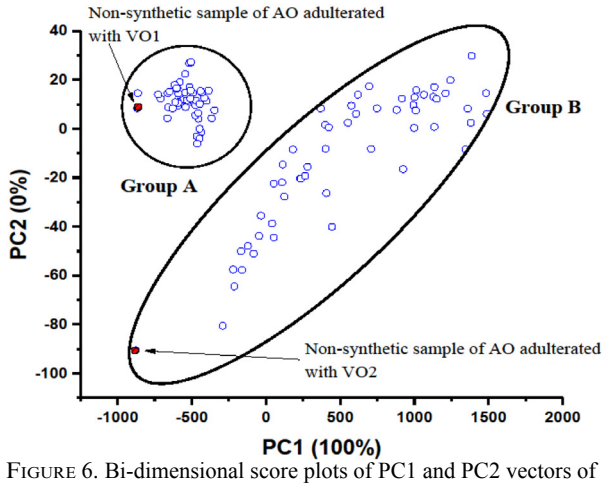

FIGURE 6. Bi-dimensional score plots of PC1 and PC2 vectors of 111 adulterated argan oil samples indicating the localization of non-synthetic samples.

PC: Principal Component.

4. CONCLUSIONS

Currently, spectroscopy techniques for food authentication are important in the food industry. In this work, it has been demonstrated that LIF spectroscopy in combination with chemometric methods (PCA and PLS) can be used as fast and nondestructive methods for the rapid detection of AO adulteration with different concentrations of cheap vegetable oil, VO1 and VO2. 54 samples were prepared containing AO adulterated by VO1 and 55 samples of AO adulterated by VO2.

PCA was applied to show the existence of spectral differences and discriminate spectral data in relation with the adulteration of argan oil with cheap vegetable oils. Samples were divided into two well-separated groups, easily allowing for the determination of the type of adulterant. It was important to use the combination of smoothing, MSC and second derivative as adequate spectral preprocessing to eliminate noise and any information that could skew the results. Then PLSR model was used to predict the amount of adulterant in argan oil. Before applying PLSR, the spectra were corrected using smoothing combined with MSC and baseline. Analyses were made on 109 samples where 70% were randomly chosen to make the calibration model, 15% for the validation and the remaining 15% for prediction sets. The calibration results produced excellent models with a correlation of 0.99, RMSEC and SEC of about 2% and for the prediction model, the correlation obtained greater than 0.92 RMSEP and about 2% SEP. The obtained models were tested using non-synthetic samples and the results were satisfactory. New samples were successfully classified according to the type of adulterant.

This study provided valuable results which could be applied to consumer protection, because the demand for high quality and safety in food production obviously calls for high standards of quality and process control. Less than 1 second LIF analysis by this model can detect the amount of adulterant in argan oil from 0.35%.

REFERENCES

Addou S, Fethi F, Chikri M, Rrhioua A. 2016. Detection of argan oil adulteration with olive oil using fluorescence spectroscopy and chemometrics tools. *J. Mater. Environ. Sci.* **7**, 2689–2698.

Callao MP, Ruisánchez I. 2018. An overview of multivariate qualitative methods for food fraud detection. *Food Control.* **86**, 283–293. http://doi.org/10.1016/j.foodcont.2017.11.034

Charlebois S, Schwab A, Henn R, Huck CW. 2016. Food fraud: An exploratory study for measuring consumer perception towards mislabeled food products and influence on self-authentication intentions. *Trends Food Sci. Technol.* **50**, 211–218. http://doi.org/10.1016/j.tifs.2016.02.003

Chikri M, Fethi F, Hamdani I, Bouyanzer A, Zarrouk A, Jama C, Costa J, Desjobert JM. 2018. Discrimination of chemical compounds of the oil of Menthasuaveolens (L.) of Eastern Morocco by the GPC-MS and chemometric methods. *J. Mater. Environ. Sci*. **9**, 909–917.

Dogruer I, Uyar H, Uncu O, Ozen B. 2021. Prediction of chemical parameters and

authentication of various cold pressed oils with fluorescence and mid-infrared spectroscopic methods. *Food Chem*. **345**, 128-815. https://doi.org/10.1016/j.foodchem.2020.128815

El Midaoui A, Haddad Y, Couture R. 2016. Beneficial effects of argan oil on blood pressure, insulin resistance, and oxidative stress in rat. *Nutrition.* **32**, 1132–1137. http://doi.org/10.1016/j.nut.2016.02.021

ELMostafi H, Bahbiti Y, Elhessni A, Bousalham R, Doumar H, Ouichou A, Benmhammed H, Touil T, Mesfioui A. 2020. Neuroprotective potential of Argan oil in neuropsychiatric disorders in rats: A review. *J. Funct. Foods.* **75**, 104-233. https://doi.org/10.1016/j.jff.2020.104233

Farres S, Srata L, Fethi F, Kadaoui A. 2019. Argan oil authentication using visible/near infrared spectroscopy combined to chemometrics tools. *Vib. Spectrosc*. **102**, 79–84. http://doi.org/10.1016/j.vibspec.2019.04.003

Garrido-Delgado R, Muñoz-Pérez ME, Arce L. 2018. Detection of adulteration in extra virgin olive oils by using UV-IMS and chemometric analysis. *Food Control.* **85**, 292–299. http://doi.org/10.1016/j.foodcont.2017.10.012

Gonzalez-Fernandez MJ, Manzano-Agugliaro F, Zapata-Sierra A, Belarbi EH, Guil-Guerrero JL. 2020. Green argan oil extraction from roasted and unroasted seeds by using various polarity solvents allowed by the EU legislation. *J. Clean. Prod*. **276**, 1–7. http://doi.org/10.1016/j.jclepro.2020.123081

Guidetti R, Beghi R, Giovenzana V. 2012. Chemometrics in food technology. *Chemometrics in practical applications*. **2012**, 217-252.

Karoui R, Blecker C. 2011. Fluorescence Spectroscopy Measurement for Quality Assessment of Food Systems-a Review. *Food Bioproc Tech*. **4**, 364–386. http://doi.org/10.1007/s11947-010-0370-0

Kharbach M, Yuc H, Kamald R, Barra I, Marmouzi I, Cherrah Y, Alaoui K, Bouklouze A, Heyden YV. 2021. New insights into the Argan oil categories characterization: Chemical descriptors, FTIR fingerprints, and chemometric approaches. *Talanta*. **225**, 122073. https://doi.org/10.1016/j.talanta.2020.122073

Majchrzak T, Wojnowski W, Dymerski T, Gębicki J, Namieśnik J. 2018. Electronic noses in classification and quality control of edible oils: A review. *Food Chem*. **246**, 192–201. https://doi.org/10.1016/j.foodchem.2017.11.013

Mazouffre S. 2009. Spectroscopie de fluorescence induite par diodes laser : Application au diagnostic des plasmas. **67**, 1–23.

Moroccan Standard. 08.5.090. 2003. Huiles d'argane. Spécifications. Service de Normalisation Industrielle Marocaine (SNIMA) Ministère de l'Industrie, du Commerce et des Télécommunications.

Morsy N, Sun D. 2013. Robust linear and non-linear models of NIR spectroscopy for detection and quantification of adulterants in fresh and frozen-thawed minced beef. *Meat Sci*. **93**, 292–302. http///doi.org/10.1016/j.meatsci.2012.09.005

Ozaki Y, McClure WF, Christy AA. 2013. Near-Infrared Spectroscopy in Food Science and Technology.

Ozulku G, Yildirim RM, Toker OS, Karasu S, Durak MZ. 2017. Rapid detection of adulteration of cold pressed sesame oil adultered with hazelnut, canola, and sunflower oils using ATR-FTIR spectroscopy combined with chemometric. *Food Control*. **82**, 212–216. http://doi.org/10.1016/j.foodcont.2017.06.034

Ruas MP, Ros J, Terral JF, Ivorra S, Andrianarinosy H, Ettahiri AS, Fili A, Van Staevel JP. 2015. History and archaeology of the emblematic argan tree in the medieval Anti-Atlas Mountains (Morocco). *Quat. Int*. **404**, 114–136. https://doi.org/10.1016/j.quaint.2015.09.030

Savitzky A, Golay MJE. 1964. Smoothing and Differentiation of Data by Simplified Least Squares Procedures. *Anal. Chem.* **36**, 1627–1639.

Şekeroğlu ZA, Aydın B, Şekeroğlu V. 2017. Argan oil reduces oxidative stress, genetic damage and emperipolesis in rats treated with acrylamide. *Biomed. Pharmacother*. **94**, 873–879. http://doi.org/10.1016/j.biopha.2017.08.034

Srata L, Farres S, Fethi F. 2019. Engine oil authentication using near infrared spectroscopy and chemometrics methods. *Vib. Spectrosc*. **100**, 99–106. https://doi.org/10.1016/j.vibspec.2018.10.002

Tipping ME, Bishop CM. 1999. Probabilistic principal component analysis. *J. R. Stat. Soc. Ser. B.* **61**, 611–622. http://doi.org/10.1111/1467-9868.00196

Ulberth F. 2020. Tools to combat food fraud–A gap analysis. *Food Chem.* **330**, 127044. https://doi.org/10.1016/j.foodchem.2020.127044

Verboven S, Hubert M, Goos P. 2012. Robust preprocessing and model selection for spectral data. *J. Chemom.* **26**, 282–289. http://doi.org/10.1002/cem.2446

Wang H, Wan X. 2020. Molecular and biomolecular spectroscopy effect of chlorophyll fluorescence quenching on quantitative analysis of adulteration in extra virgin olive oil. *Spectrochim. Acta Part A Mol. Biomol. Spectrosc*. **248**, 119183. http://doi.org/10.1016/j.saa.2020.119183

Wold S, Trygg J, Berglund A, Antti H. 2001. Some recent developments in PLS modeling. *Chemom. Intell. Lab. Syst.* **58**, 131–150. https://doi.org/10.1016/S0169-7439(01)00156-3

Xing C, Yuan X, Wu X, Shao X, Yuan J, Yan W. 2019. Chemometric classification and quantification of sesame oil adulterated with other vegetable oils based on fatty acids composition by gas chromatography. *Lwt*. **108**, 437–445. https://doi.org/10.1016/j.lwt.2019.03.085

Yang H, Irudayaraj J, Paradkar MM. 2005. Discriminant analysis of edible oils and fats by FTIR, FT-NIR and FT-Raman spectroscopy. *Food Chem*. **93**, 25–32. http://doi.org/10.1016/j.foodchem.2004.08.039

Zheng KY, Zhang X, Tong PJ, Yao Y, Du YP. 2015. Pretreating near infrared spectra with fractional order Savitzky-Golay differentiation (FOSGD). *Chinese Chem. Lett*. **26**, 293–296. http://doi.org/10.1016/j.cclet.2014.10.023